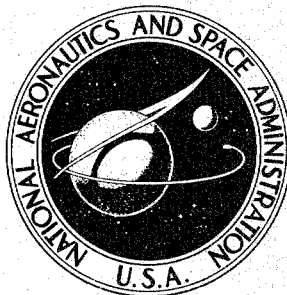
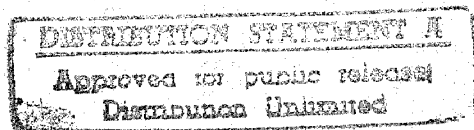


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**AN EXPERIMENTAL FEASIBILITY
STUDY FOR THE PREPARATION OF
THERMO-OXIDATIVELY STABLE
PYRRONE LAMINATES**

*by H. R. Lubowitz, R. J. Jones, H. N. Cassey,
R. W. Vaughan, and E. A. Burns*

*Prepared by
TRW SYSTEMS
Redondo Beach, Calif.
for Langley Research Center*

**DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATINNY ARSENAL, DOVER, N. J.**

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Redondo Beach, Calif.

for Langley Research Center

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

FOREWORD

This document constitutes the final report for the work accomplished between 2 August 1968 and 2 December 1968 by TRW Systems for the National Aeronautics and Space Administration, Langley Research Center, under Contract NAS1-8384 on An Experimental Feasibility Study for the Preparation of Thermo-oxidatively Stable Pyrrone Laminates.

The work was under the technical direction of Dr. Vernon E. Bell of the Langley Research Center, Hampton, Virginia.

The Chemical Research and Services Department of the Chemistry and Chemical Engineering Laboratory, Science and Technology Division was responsible for the work performed on this program. Mr. B. Dubrow Manager, Chemistry and Chemical Engineering Laboratory provided overall program supervision, Dr. E. A. Burns was Program Manager and Mr. H. R. Lubowitz was Principal Investigator. Acknowledgment is made of the technical assistance provided during this program by the following TRW Systems personnel:

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ABSTRACT

◀ This report describes the preparation of Pyrrone laminates, from a sulfone dianhydride, which would be suitable for long-term exposure to extreme thermal and oxidative environments. ▶ The work was divided into three principal tasks: (1) monomer synthesis, (2) polymer synthesis and characterization, and (3) laminate processing and evaluation.

Pyrrone resins were prepared from bis (3,4-dicarboxyphenoxyphenyl) sulfone dianhydride and 3,3'-diaminobenzidine. Suitable conditions were determined for preparing laminates from completely soluble Pyrrone precursors. ◀ The laminates, which were made under relatively mild processing conditions, had medium void content and had mechanical properties similar to other state of the art condensation polymers.

Laminates were subjected to long term exposure in forced air environments representing extreme end use thermo-oxidative conditions. The Pyrrone composites demonstrated resistance to the oxidative environment, but gradually succumbed under the conditions employed. The aging data were used to predict useful life durations for specimens tested. 7

The experimental feasibility study has given results that demonstrate several interesting features of the Pyrrone films and laminates prepared from bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride and 3,3'-diaminobenzidine. This resin gave neat resin and composite properties similar to or exceeding those published for state of the art Pyrrone polymer systems.

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TRW SYSTEMS

1. INTRODUCTION AND SUMMARY

This report describes a 4-month experimental feasibility study on the preparation of thermo-oxidatively stable Pyrrone laminates. The study was divided into three principal research tasks:

- Monomer synthesis
- Varnish synthesis and characterization
- Laminate processing and evaluation

Varnish synthesis and laminate processing depended on the successful laboratory production of sufficient quantities of BSDA monomer of polymer grade purity. First, attempts were made to scale up the synthesis of BSDA by previously developed TRW technology. The scale-up successfully produced material with good stoichiometry and high yields, but the purity was too low. Improved synthesis and purification steps were then adopted which led to the production of BSDA monomer in adequate polymer grade purity. The purified product was then used to produce reproducible varnish solutions of amic-acid-amine (A-A-A) for subsequent resin film studies and laminate processing studies.

Polymer grade BSDA and DAB were used to prepare varnish solution of A-A-A polymers in DMF. All A-A-A polymers produced in this study were completely soluble in solution. The varnish solutions prepared were characterized as to relative viscosity to develop varnish viscosity - polymer molecular weight relationships. Tough, flexible A-A-A films were routinely produced during this study by casting directly from the DMF varnish solutions. These films were used to assess the properties of BSDA-DAB derived A-A-A polymer and Pyrrones. The A-A-A

films were used to define conditions necessary for removal of water of condensation necessary for the production of the desired pyrrone ladder-type polymer backbone linkage. The Pyrrone films prepared were studied for tensile properties, thermal and oxidative properties, and long term aging characteristics.

The varnish synthesis methods developed were used to prepare varnish in quantities sufficient for undertaking laminate processing studies. The drying conditions necessary for removal of DMF from resin were used to prepare Style 181 E glass prepreg cloth containing BSDA-DAB A-A-A resin. The complete solubility of polymer in DMF allowed the impregnation of reinforcing cloth to be readily accomplished using simple hand dip procedures. Resin flow studies gave early indication of potential mild laminate processing conditions. Several experimental investigations established that adequate resin flow of approximately 10% could be accomplished employing 200 psi pressure and 600°F temperature. The flow studies also established the BSDA-DAB resin to have a highly desired finite gel time of up to 30 seconds.

The results of the flow studies were used to prepare several laminate samples employing mild processing conditions. It was determined experimentally that processing conditions consisting of a 15-second dwell time at 600°F followed by a two-hour cycle at 600°F and a one-hour cycle at 700°F, both at 200 psi, were sufficient to give low void content specimens possessing encouraging mechanical properties. The void contents of all samples produced ranged from 7 - 16%, while mechanical properties consistently included flexural strengths of approximately 50 Kpsi and flexural moduli nearing 3 Mpsi. These properties, obtained for an experimental resin/laminate system in the early stage of development, are considered to be excellent and permitted undertaking post curing studies and laminate air-aging studies.

It was determined that post cure of the processed laminates is necessary to prepare specimens capable of enduring long term exposure to thermo-oxidative environments of $\geq 600^{\circ}\text{F}$. Several laminate samples were aged in forced air at 600°F and 700°F to establish the long term oxidative stability of the BSDA-DAB Pyrrone E glass reinforced system.

Samples having been exposed to a 750^oF post cure at 200 psi in the press displayed the greatest resistance to degradation in an oxidative environment. Useful laminate property lives of up to 280 hours in air at 600^oF were established.

2. VARNISH SYNTHESIS STUDIES

Varnishes of amic-acid-amine (A-A-A) polymers derived from bis(3,4-dicarboxyphenoxyphenyl)sulfone dianhydride (BSDA) and 3,3'-diaminobenzidine (DAB) in dimethylformamide (DMF) were prepared and characterized for subsequent use in the preparation of reinforced Pyrrone laminates. An integral part of this work required the development of routine reproducible laboratory procedures for the preparation of bis(3,4-dicarboxyphenoxyphenyl)sulfone dianhydride (BSDA) to polymer grade purity. The A-A-A varnishes were prepared by reacting BSDA with DAB in DMF under a variety of experimental conditions to prepare completely soluble polymer solutions. The A-A-A polymers were cast as thin films directly from the DMF reaction solutions and the films were employed to conduct Pyrrone curing studies and polymer characterization.

2.1 BIS(3,4-DICARBOXYPHENOXYPHENYL) SULFONE DIANHYDRIDE SYNTHESIS STUDIES

An integral requirement of this project was the availability of BSDA in sufficient quantities of polymer grade material to allow the experimental varnish synthesis and laminate studies to be completed. The laboratory synthesis of BSDA was accomplished according to the following reaction shown in Figure 1. Upon initiation of the contract experimental work, it was found that BSDA prepared from as-received monomers did not yield A-A-A polymer in DMF unless an unreasonable excess ($\geq 50\%$) of dianhydride was employed. This was attributed to impurities introduced on scale-up of the dianhydride synthesis—a plague common to many multi-step organic synthesis reactions. Scale-up was a necessity due to the relatively large quantities of material required by the various project tasks. The impurity problem was immediately attacked with a three-pronged effort:

- Recrystallization of all monomers and intermediate products.
- Development of mild work-up conditions to avoid any tetraacid decarboxylation
- Laborious water-treatment (leach) of tetraacid and dianhydride to remove occluded salts.

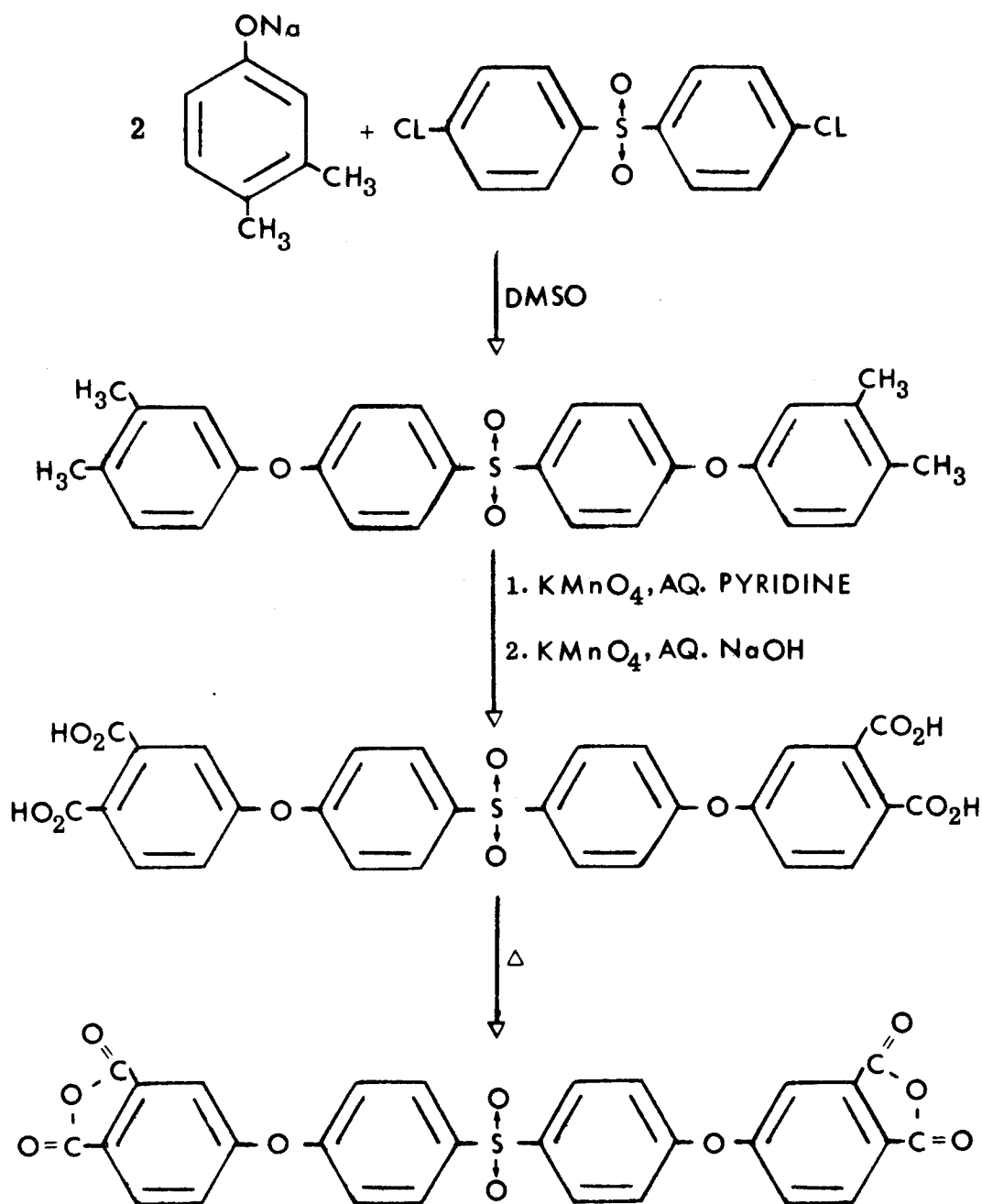


Figure 1. Reaction Sequence Employed for the Laboratory Synthesis of Bis(3,4-dicarboxyphenoxyphenyl) Sulfone Dianhydride (BSDA)

The improved synthetic procedures included incorporation of the following steps:

Twice recrystallized bis(4-chlorophenyl) sulfone was allowed to react with sodium 3,4-xylenolate prepared from twice recrystallized 3,4-xylenol in dimethyl sulfoxide (DMSO). These reactants were allowed to stir for periods of 72-120 hours to define the desired bis(3,4-dimethylphenoxyphenyl) sulfone in yields of 90% or greater. The bis(3,4-dimethylphenoxyphenyl) sulfone was then recrystallized twice from isopropanol to give material possessing a sharp melting point. The recrystallized tetramethyl product was then subjected to a two-stage oxidation which first employed potassium permanganate and a pyridine-water solution to give a crude partially oxidized product. This partially oxidized product was then used directly for the second oxidation employing potassium permanganate in aqueous sodium hydroxide solution. The crude tetraacid was isolated by acidification with cold, dilute hydrochloric acid to avoid decarboxylation. The crude acid was then heated at 120-180° to form crude BSDA. The crude dianhydride was converted to polymer grade material by subjecting it to a water leach procedure in which the BSDA was either 1) boiled in distilled water for a short time or 2) leached by stirring at room temperature in distilled water.

2.2 VARNISH SYNTHESIS STUDIES

The preparation of BSDA in polymer grade and in sufficient quantities allowed TRW to initiate an intensive study into the preparation of the A-A-A Pyrrone precursor. Being cognizant of the importance of using dry polymerization solvents in such studies, all DMF employed throughout the studies was distilled from molecular sieves and subsequently stored over fresh sieves. TRW employed all glass polymerization equipment for the A-A-A synthesis studies. A typical set up is illustrated in Figure 2. The glassware was always freshly dried in an oven prior to use. The experiment procedure followed involved addition of BSDA solution in DMF to a stirred solution of 3,3'-diaminobenzidine (DAB) (Burdick and Jackson) in DMF under a nitrogen blanket. The technique (Reference 1) of fast addition of approximately 90% of the BSDA solution, followed by dropwise addition of the remainder was employed.

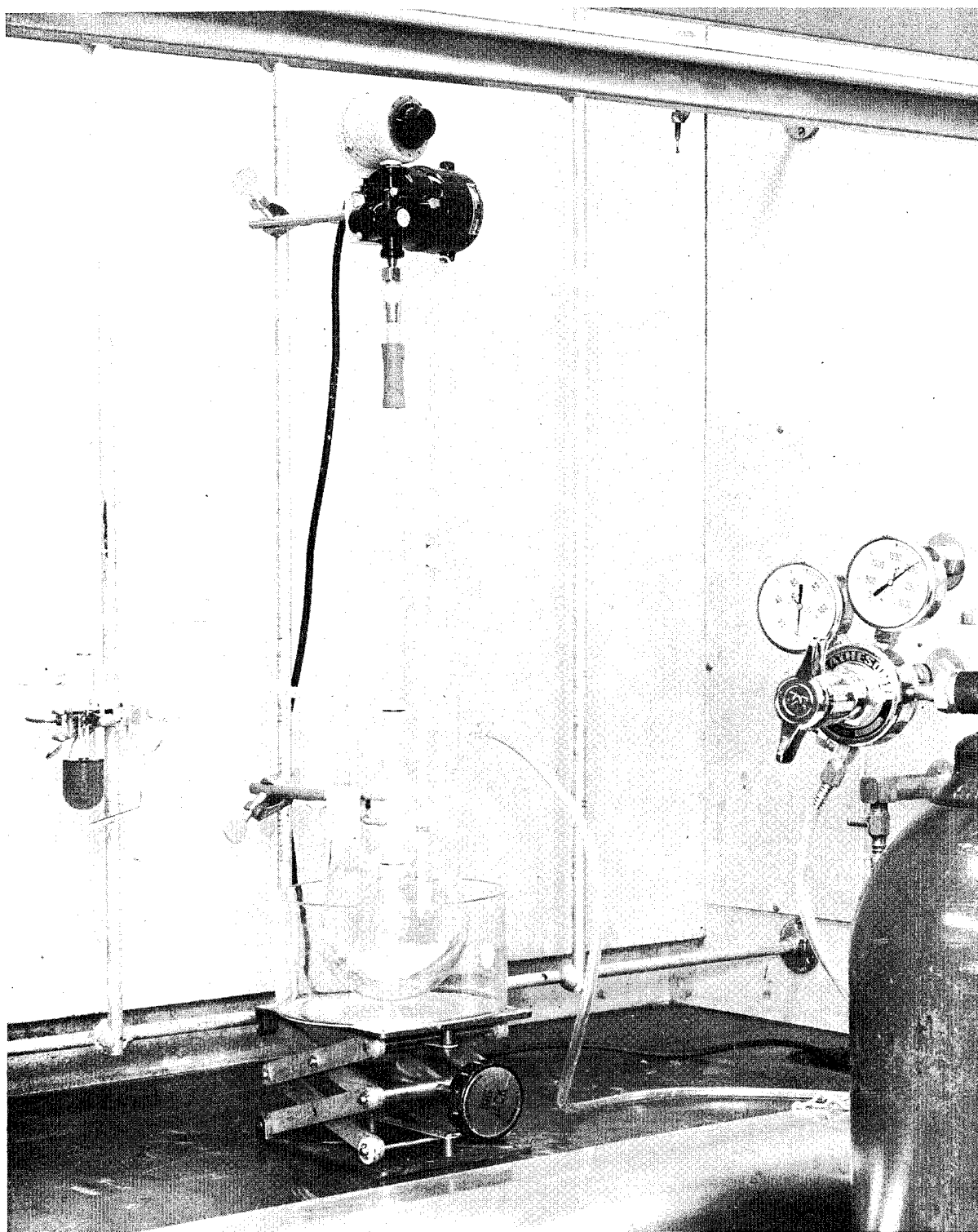


Figure 2. Varnish Synthesis Apparatus

Early in the varnish studies, attempts were made to define maximum limit of solubility of the BSDA-DAB A-A-A polymer. These experiments showed that the maximum solubility of BSDA in DMF was 28%. Initial polymerization studies, therefore, employed a 25% w/w ratio of reactants in DMF to experiment on A-A-A solubilities at this concentration. These experiments were successful and A-A-A polymer capable of being cast directly onto glass plates employing a doctor's knife produced tough, flexible films on solvent drying. Several runs were made at a 25% w/w reactants solid loading in DMF in which varying amounts of excess BSDA (5-10%) were employed. The molecular weight of polymer was allowed to build up over long stirring periods to give the data from which the set of curves appearing in Figure 3 were derived. Because of the possibility that the 25% w/w solution concentrations were too high and limited rapid chain growth, it was decided to determine the affect of lower monomer concentration (c.a. 20% w/w) on molecular weight buildup in DMF. The data obtained in these similar studies are displayed graphically in Figure 4. Because of no apparent differences in molecular weight at the two concentration studied, the lower concentration (c.a. 20% w/w) was employed in all subsequent A-A-A varnish runs because of easier handling.

The initial varnish studies pointed out two major features of the TRW BSDA monomers. It was shown that the BSDA skeleton containing oxygen and sulfone linkages gives A-A-A polymers (η_{inh} up to 0.3) that possess a high degree of solubility in DMF. This strong solubility attribute was utilized to the fullest in the laminate processing studies (described later in Section 3) in which reinforcement prepregging was accomplished with minimum difficulty.

The other significant result from the BSDA-DAB A-A-A studies is the slow rate of reactivity of the TRW dianhydride. Figures 3 and 4 show the continuous buildup of relative solution viscosity regardless of concentration. The reason for the slow reactivity of BSDA in DMF has not been clearly established, although a reasonable explanation of the behavior could be high solvation of both BSDA monomer and growing A-A-A chains by DMF which limit the reactivity of this high molecular weight species in solution, and consequently cause slow rates of polymerization.

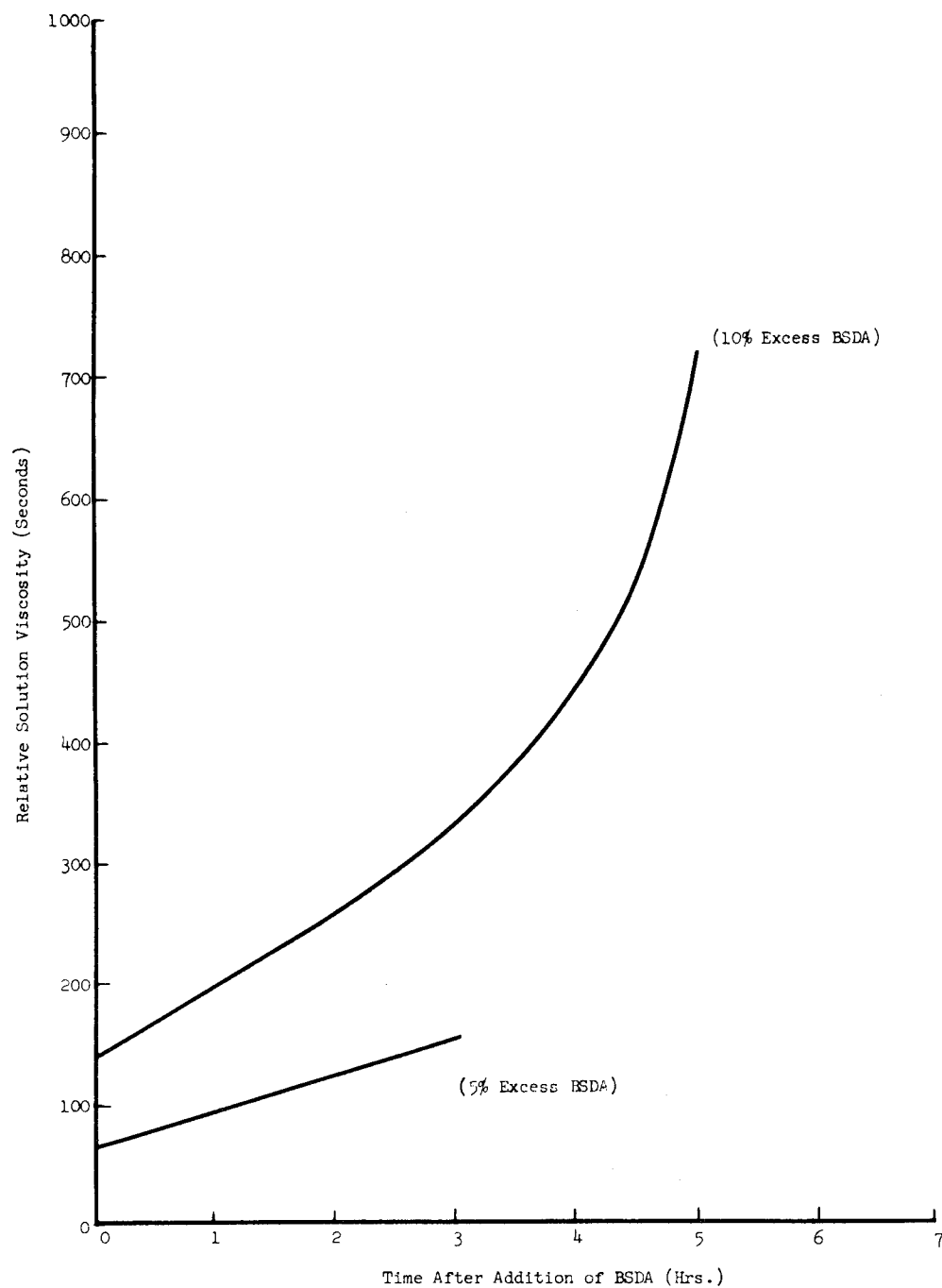


Figure 3. Varnish Solution Viscosity Build-up as a Function of Stirring Time (25% w/w Concentration of BSDA and DAB in DMF)

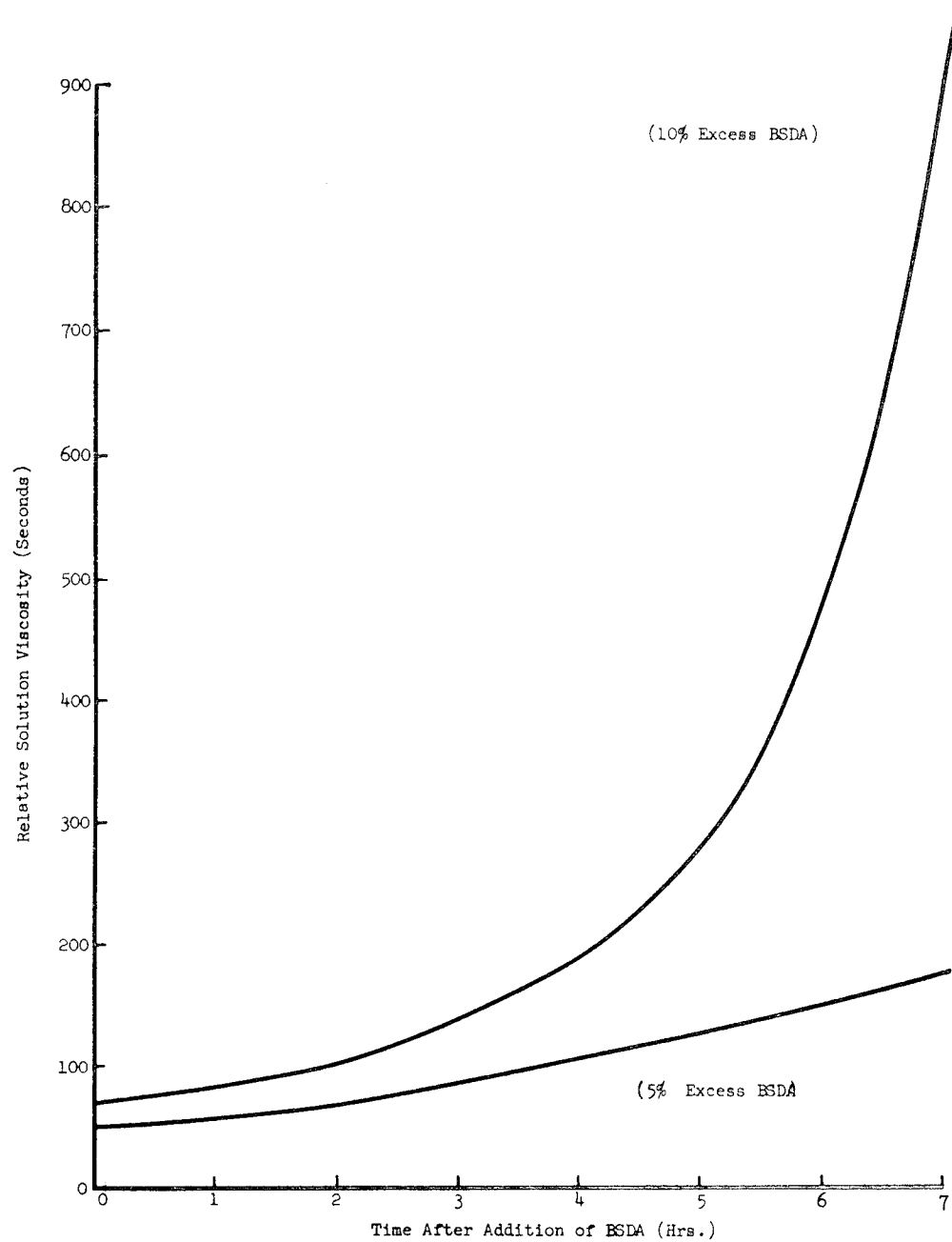


Figure 4. Varnish Solution Viscosity Build-up as a Function of Stirring Time (20% w/w Concentration of BSDA and DAB in DMF)

The molecular weights ($\eta_{inh} \sim 0.3$) of A-A-A polymer described above were used for film curing studies discussed below and laminate preparation studies described in Section 3.

The A-A-A varnish solutions described previously were used to cast tough, flexible films suitable for employment in curing studies to determine conditions necessary for A-A-A ring closure to the ladder-type Pyrrole linkage. Initial conditions for the study employed thermal cycles similar to those reported in the literature (References 2 and 3).

It was determined experimentally that the most satisfactory drying temperature for DMF removal from cast A-A-A films was one-half hour at 125°C under vacuum or in a forced air oven. These conditions were selected on the basis of a combination of film properties (e.g., flexibility, uniformity, absence of solvent, etc.). The dried A-A-A films gave infrared spectrum shown in Figure 5 and major absorptions tabulated in Table I. Having ascertained that the films possessed the desired A-A-A structure, samples were cured in a two-step method to form the Pyrrole linkage.

TABLE I
PRINCIPLE A-A-A AND PYRROLE INFRARED ABSORPTION DATA

Band, cm^{-1}	Assignment	A-A-A	Pyrrole
1772		Medium	Absent
1755	-CON<	Absent	Strong
1730	-CON<	Absent	Strong
1712	-COO-	Strong	Absent
1660	-CONH-	Strong	Absent
1615	-C=N-	Weak	Strong
1405	-COOH	Weak	Absent
1262	-COOH	Weak	Absent
964	-COOH	Weak	Absent
935		Absent	Weak
745		Medium	Absent
728	-CON<	Very Weak	Weak
658		Weak	Absent
620		Very Weak	Weak

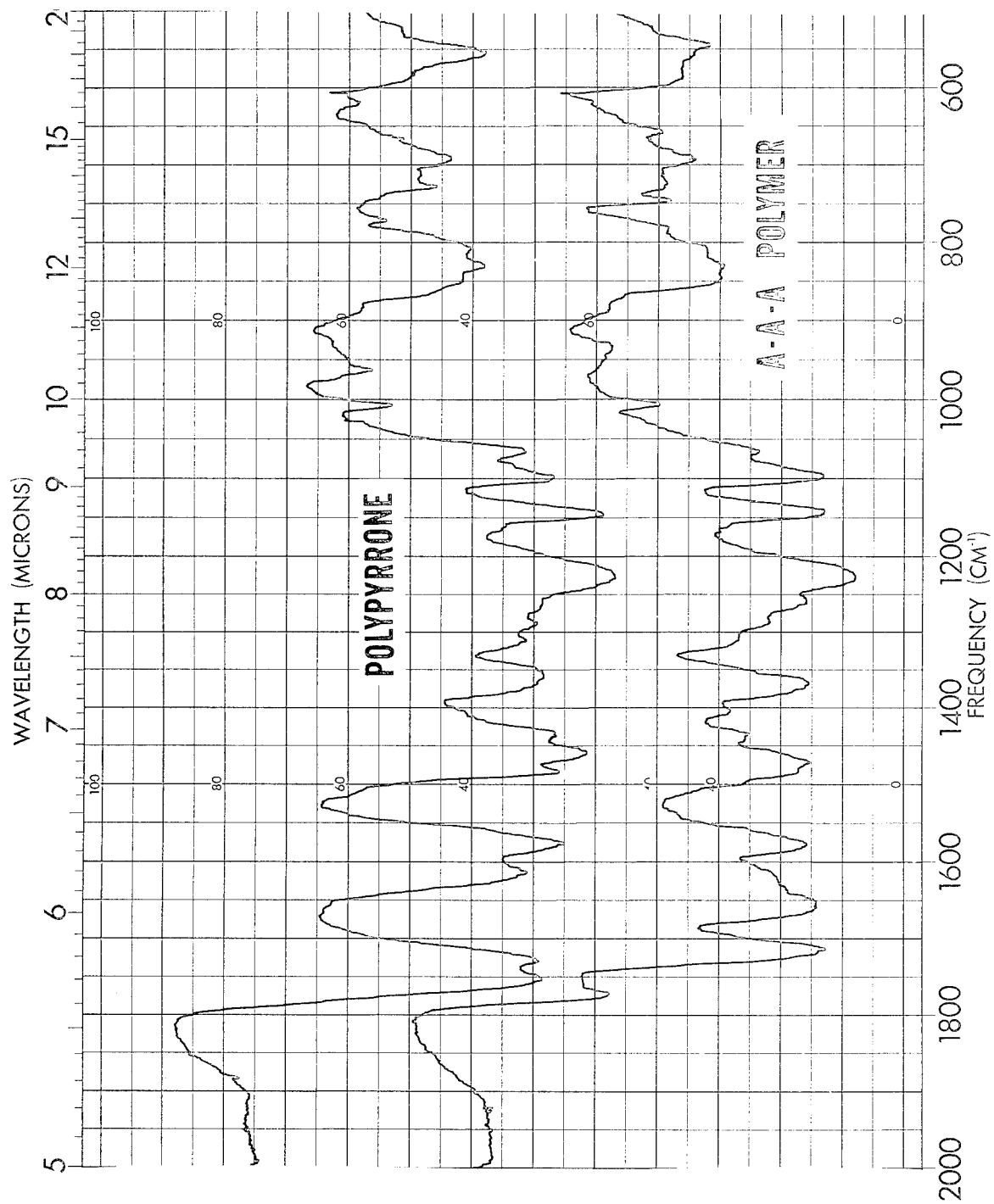


Figure 5. Comparison of A-A-A Polymer and Pyrrone Infrared Spectra

First, several thermal cycles were investigated to determine if the route to form the Pyrrone linkage went through the preferred imide amine (IA) backbone linkage intermediate. It was found that oven heating (either in nitrogen or under vacuum) at 200 - 250°C was sufficient to give the desired partial ring closure to IA as indicated by infrared spectral evidence. The IA first stage cured films were, as expected, less flexible than their A-A-A precursors.

The first stage cured IA films were then subjected to second stage curing studies to define complete ring closure by Pyrrone formation. A variety of experimental second stage curing conditions, employing temperatures from 300 - 400°C for several hours, established a four-hour cure under vacuum at 350 - 360°C to give the best Pyrrone product. This judgment was based on the combination of film properties (e.g., flexibility, uniformity, infrared ring closure and weight retention on aging at 700°F). The films obtained were dark amber to red in color and, of course, more brittle than their A-A-A or IA precursors. A representative Pyrrone infrared spectrum appears in Figure 5 with absorption data given in Table I.

Additional varnish and film data including those for the BSDA dianhydride, DMF A-A-A varnish solutions and A-A-A and cured films are presented in the Appendix. All processing information derived in the varnish synthesis studies provided guidance and a starting point in the laminate processing studies.

3. LAMINATE PROCESSING STUDIES

The data generated during the varnish synthesis studies were directly applied to the preparation of BSDA-DAB derived pyrrone laminates. Scaled up quantities of the A-A-A varnish solutions were prepared and were used to impregnate Style 181 E glass coated with A-1100 amino-silane finish. This reinforcement material was employed throughout the laminate processing studies. Descriptions of these sequential activities are presented below.

3.1 IMPREGNATION STUDIES

A-A-A varnish solutions (DMF) of 20% w/w solids loading were employed to impregnate Style 181 E glass cloth under a variety of conditions. The 125°C (~250°F) drying temperature established as optimum for film drying proved to be too severe for prepreg drying and advanced the resin to partial IA which caused difficulty in subsequent processing. It was found that a 200°F (93°C) drying cycle for 15 minutes in a forced air oven gave preregs having the desired approximate 10% volatile content, used as a standard in laminate preparation. As part of the same study, it was determined experimentally that a hand dip method of preparing preregs (two to three passes) gave the desired resin pickup (30-40% w/w) as determined by resin burnoff experiments. These hand dip and resin pickup data were determined on DMF varnish solutions of 250-500 centipoise viscosity containing A-A-A polymer of $\eta_{inh} \sim 0.3$.

3.2 RESIN FLOW STUDIES

A-A-A prepregged Style 181 E glass cloth, prepared according to conditions defined in the impregnation studies were used to obtain resin flow data necessary to establish preliminary laminate processing conditions. The press temperature chosen for these studies was 600°F, a standard for state of the art experimental resin work and a temperature below which Pyrrone ring closure occurred ($\geq 700^\circ\text{F}$ as defined for film studies). As is standard for flow studies, no contact dwell time in the press was employed.

The results of the flow studies were quite gratifying. It was established that a 200 psi pressure at 600°F was sufficient to give 8-12% flow

for prepreg samples of ~32% resin content. These flow studies gave evidence that the BSDA-DAB polymer system was, as speculated, a resin that could be processed to Pyrrone under conditions considered to be "very mild" for such a highly stiff, ladder type polymer. Flow specimens prepared gave a high hardness, 50-60 Barcol. Another significant data point determined during this flow study was that the BSDA-DAB gel time had a finite duration of 15-20 seconds, as determined from A-A-A varnish solution applied directly to press platens at 600°F.

3.3 LAMINATE PREPARATION

The impregnation and flow study data were used directly to prepare a number of intermediate size laminate samples. It was desired during this experimentation to prepare several 1/8-inch thick (13 prepreg plies) structures of sufficient size (5-inch x 6-inch) to cut into three equal portions for mechanical property determinations at room temperature, as well as after aging at 600°F and 700°F in air.

The experimental technique employed for the laminate preparation studies involved a finite prepreg dwell time of 15 seconds at 600°F in the press, followed by application of 200 psi pressure for two hours while maintaining 600°F thermal environment and one hour at 700°F. These conditions were followed for all laminate samples prepared.

The effect of post cure on the mechanical properties was investigated experimentally. Post cure condition variables studied included time, and temperatures both under static nitrogen and under pressure. All methods tried defined compact, good-looking composite structures of high hardness, approaching 75 Barcol as a maximum. The exact post curing methods were dictated by results of aging in air at 600°F. The mechanical properties of the post cured laminates are given in Table II.

The laminate post curing studies in the press employed temperatures from 700-750°F for time periods up to four hours. The 750°F cured specimens were black in color (vs brown for the one sample post cured at 700°F) and gave indication of very few microcracks from end-on viewing under a microscope. These black, post cured samples gave calculated void contents of 7-9%, quite low for a condensation-type resin-based laminate in the early stage of development.

TABLE II
LAMINATE PROCESSING^a AND CHARACTERIZATION DATA

Specimen Size as Molded	Press Conditions Cure Time/ Temperature	Post Cure Conditions	Average Resin Content % w/w	Average Specific Gravity	Average Void Content % v/v	Mechanical Properties	
						Average Modulus/ Room Temp	Flexural Strength/Shear Strength After 600°F Aging
1. 3" x 6" 8 plies	1 hr at 600°F 1 hr at 700°F	None	46.5	1.83	6.7	53 Kpsi/ 2.9 Mpsi/ 4.2 Kpsi	---
2. 5" x 6" 13 plies	2 hrs at 640°F 1 hr at 710°F	1/2 hr at 740°F (press)	27.1	1.79	14.6	53 Kpsi/ 2.7 Mpsi/ 1.9 Kpsi	b
3. 5" x 8" 13 plies	2 hrs at 600°F 1 hr at 700°F	None	25.0	---	---	53 Kpsi/ 2.9 Kpsi/ ---	c
4. 5" x 6" 13 plies	2 hrs at 600°F 1 hr at 700°F 1/2 hr at 750°F	f	32.4	1.85	8.8	f	
(a)	2 hrs at 600°F 1 hr at 700°F 1/2 hr at 750°F	24 hrs at 600°F 24 hrs at 650°F 24 hrs at 700°F 6 hrs at 750°F (N ₂)	26.1 ^d	1.99 ^d	8.8 ^d	---	6.8 Kpsi/ ^d 1.2 Mpsi/ 1.0 Kpsi
(b)	2 hrs at 600°F 1 hr at 700°F 1/2 hr at 750°F	4 hrs at 750°F (press)	22.6 ^e	1.97 ^e	9.1 ^e	---	14.9 Kpsi/ ^e 1.9 Mpsi/ 1.1 Kpsi

^aAll samples molded at 200 psi

^bAged sample gave 0 resin after 400 hours aging in air at 600°F

^cAged sample gave 0 resin after 200 hours aging in air at 600°F

^dProperties determined after 48 hours aging in air at 600°F

^eProperties determined after 72 hours aging in air at 600°F

^fSample retained for NASA Langley Project Manager

The void content values given in Table II show the development of an interesting trend. At this early stage of laminate development work, it certainly appears that resin contents approaching 35-40% are required to produce compact structures of low void content.

Also important in examination of the data in Table II are the results for sample 4a and 4b which were subjected to the two different post cure methods commonly practiced in laminate processing. Sample 4b post cured in the press at 750°F at 200 psi gave much higher mechanical property data on aging at 600°F than sample 4a, prepared from the same laminate specimen, but postcured outside of the press under nitrogen. This particularly significant because of the longer aging duration of sample 4b at 600°F in air.

3.4 LAMINATE AGING STUDIES

The laminate samples prepared were subjected to long term aging under a current of air in forced air ovens at 600°F and 700°F. In each case the specimens were positioned in the oven so as to provide direct exposure of the full flow of hot forced air. The results of the 600°F, forced air aging are presented in graphic form in Figure 6. In no case did any of the prepared samples endure these conditions for the planned 500 hours. One practical rule of thumb often used in relating resin weight loss to laminate properties is that the time at which 50% of the resin has been consumed approximates the useful life of the laminate (c. a. 10 Kpsi flexural strength). On this basis, it is seen that feasibility for useful life of about 280 hours was demonstrated by laminate 2. This laminate sample had a 25% resin content and was post cured at 750°F which suggests the direction of post curing conditions necessary for further improvement in properties. Comparable testing of a non-post cured laminate (Sample 3) at 700°F showed a useful life (50% resin weight retention) of 40 hours.

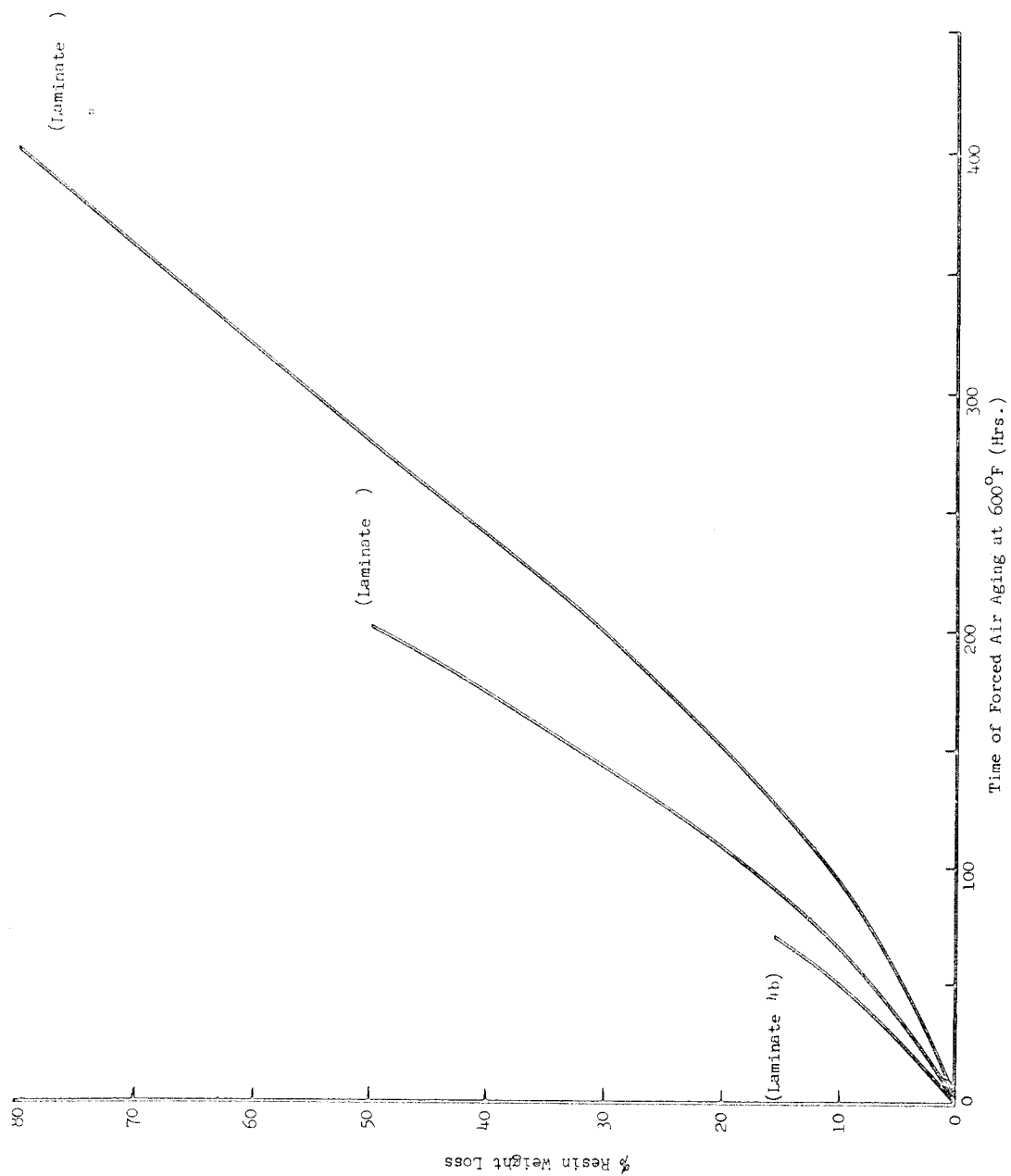


Figure 6. Laminate Resin Weight Loss as a Function of Duration of Forced Air Aging at 600°F

4. CHARACTERIZATION

The methods used for obtaining sample property data appearing in this report are described below.

4.1 BIS(3,4-DICARBOXYPHENOXYPHENYL) SULFONE DIANHYDRIDE (BSDA)

The samples of BSDA prepared by synthesis during this feasibility study were characterized as follows:

- Capillary melting point - MEL-TEMP MF Laboratory Devices.
- Differential Scan Calorimetry - Perkin Elmer Model DSC-1.
- Dianhydride equivalence number - meq/g based on back-titration technique employing standardized solutions of sodium hydroxide and hydrochloric acid.

4.2 VARNISH SYNTHESIS STUDIES

The dimethylformamide A-A-A varnish solutions and film products produced from these varnish samples were characterized by the following methods:

- Relative varnish solution viscosities - time in seconds required for 1 ml flow in a capillary pipet.
- Inherent viscosities - determined using 0.5% w/v solutions in DMF at $25 \pm 0.2^{\circ}\text{C}$ employing a Cannon-Fenske type viscometer.
- Infrared analysis - Perkin Elmer Model 521.
- Thermogravimetric analysis - Aminco Thermo-Grav, heating rate $3^{\circ}\text{C}/\text{min.}$, 100 ml/min gas flow.

4.3 LAMINATE PROCESSING STUDIES

The data reported for all varnish solutions, Style 181 E glass prepreg and laminates were determined as follows:

- Viscosity Measurements - Brookfield viscometer Model LVT-17526.
- Volatile contents - obtained by heating at 350°F and 700°F for 10 minutes, FTM-406-6081.

- Resin contents - determined after burnoff at 600°C for two hours in a muffle furnace in air, FTM-406-7061.
- Flow - determined from weight loss obtained at fixed pressure and 600°F employing a press with no dwell time, FTM-406-2041.
- Specific gravity - FTM 406-5011.
- Void content - calculated employing MIL-P-17549C.
- Laminate preparation - prepared employing a Pasadena Hydraulic Incorporated Model SP 215C at reported temperatures and 200 psi.
- Flexural properties - determined on 1/2-inch x 4-inch test specimens on Instron Model TTCLM No. 1.6, ASTM D 790.
- Interlaminar shear strength - determined according to short beam method ASTM D 2344.
- Laminate aging - specimens aged in forced air oven at reported temperatures.

5. CONCLUSIONS

The results of this experimental feasibility study for the preparation of thermo-oxidatively stable Pyrrone laminates have been reviewed and assessed. The major conclusions from this evaluation are summarized below for resins and laminates prepared from bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride (BSDA) and 3,3'-diaminobenzidine (DAB).

1. The polyamic-acid-amine polymers prepared from BSDA and DAB are soluble to $\geq 25\%$ w/w in dimethyl formamide. The resulting low molecular weight ($\eta_{inh} < 0.3$) varnish solutions can be directly applied in prepreg formation.
2. The room temperature Pyrrone film and laminate mechanical properties produced from this resin system are promising.
3. The resin system can be processed under mild conditions, considering the rigid backbone structure and condensation volatiles produced.
4. The calculated void contents of approximately 7% (at laminate specific gravities near 2.0) are as good or better than those produced by similar state of the art condensation polymers.
5. The BSDA monomer appears to have a very slow rate of reactivity in DMF with DAB, even at excesses above equivalence.
6. The direction for improvement of long term thermo-oxidative stability of Pyrrone laminates at $\geq 600^{\circ}\text{F}$ has been identified.

APPENDIX

This Appendix provides detailed representative experimental procedures employed by TRW during this feasibility study effort. The outlined experiments were carried out according to procedures discussed in general in Sections 2 and 3. The characterization equipment and methods employed are outlined in Section 4.

A. 1 VARNISH SYNTHESIS STUDIES

A. 1. 1 Synthesis of Bis(3,4-dicarboxyphenoxyphenyl) Sulfone Dianhydride (BSDA)

The following procedure described were used to prepare polymer grade BSDA as well as its immediate precursors.

A. 1. 1. 1 Synthesis of Bis(3,4-tetramethylphenoxyphenyl) Sulfone - In a 5-liter 3-necked round-bottomed flask (equipped with a reflux condenser, thermometer, and an inlet for nitrogen purge) was placed a mixture of 287 g (1.0 mole) of bis(4-chlorophenyl) sulfone (K and K Laboratories; recrystallized twice from isopropanol m.p. 132-133°C), 343 g (2.2 moles) of sodium 3,4-xylenolate (prepared from J. T. Baker 3,4-xylenol recrystallized twice from benzene, xylenol m.p. 65-66°C), 1000 ml of dimethyl sulfoxide (Crown-Zellerbach) and 192 ml of chlorobenzene (Eastman). This mixture was stirred magnetically and heated at 120°C for a period of 96 hours. The resulting dark brown reaction solution was poured, with stirring, into five gallons of iced distilled water. The crude product was isolated by vacuum filtration and dried at 100°C under vacuum to give 414 g (90%) of a brown powder. The crude product was recrystallized twice from isopropanol to give white needles; m.p. 131-133°C.

A. 1. 1. 2 Synthesis of Bis(3,4-dicarboxyphenoxyphenyl) Sulfone - In a 12-liter, 3-necked round-bottomed flask (equipped with a reflux condenser mechanical stirrer, and thermometer), was placed a mixture of 297.6 g (0.64 mole) of recrystallized bis(3,4-dimethylphenoxyphenyl) sulfone (prepared as described above), 3200 ml of pyridine (J. T. Baker - reagent grade), and 1600 ml of distilled water. This mixture was refluxed at 94°C for a period of four hours, during which time 445 g (2.6 moles) of potassium permanganate (J. T. Baker, reagent grade) was added in small portions. After complete addition of permanganate, refluxing was continued

for a period of ten hours. The resulting dark brown reaction mixture was filtered hot under vacuum to remove precipitated manganese dioxide. The crude, partially oxidized product was isolated by evaporation of the aqueous pyridine solvent on a rotary evaporator. The crude, basic soluble product obtained above was placed in an apparatus identical to that described. To this material was added 4000 ml of 1.8N sodium hydroxide solution and 1600 ml of distilled water. The resulting solution was stirred and refluxed for four hours, during which time 600 g (3.5 moles) of potassium permanganate (J. T. Baker, reagent grade) was added as a solid in small portions. After complete addition of the potassium permanganate, stirring at reflux was continued for six hours. Any unreacted oxidizing agent was inactivated by the addition of 40 ml of ethanol and then the reaction mixture was filtered hot under vacuum to remove manganese dioxide. The straw yellow filtrate was boiled to remove any unoxidized ethanol. The boiled filtrate was then placed in a 12-liter flask and cooled to 5°C. To this cooled filtrate was added cold, dilute (0.6N) hydrochloric acid, with stirring until the pH reached 2 (Hydrion paper). The crude reaction product was isolated by filtration under vacuum and washed with several portions of cold distilled water until the filtrate gave a reading of pH 5.

A. 1. 1. 3 Conversion to Bis(3,4 -dicarboxyphenoxyphenyl) Sulfone

Dianhydride - The crude tetraacid obtained as above was converted to dianhydride by heating at 180°C for four hours under vacuum, which gave 100 g (75%) of crude product:

Titration (equivalent weight); Theoretical: 135.6 meq/g

Found: 160 meq/g

The crude bis(3,4-dicarboxyphenoxyphenyl) sulfone dianhydride was placed in a 2-liter beaker and boiled for one-quarter hour in distilled water. The mixture was filtered hot under vacuum and dried at 180°C under overnight in a vacuum oven. This water leached product was characterized as follows:

Melting point: Capillary, 247-251°C

DSC, 251.5°C

Titration (eq. weight); Theoretical: 135.6 meq/g

Found: 134.0 meq/g ave

A.1.2 Polymer Investigation

A.1.2.1 Preparation of Amic-Acid-Amine - In a 100-ml three-necked, round-bottom flask, equipped with a 50-ml dropping funnel, thermometer, mechanical stirrer, and a nitrogen purge inlet (See Figure 1, for a similar set-up), was placed 2.14 g (0.010 mole) of 3,3'-diaminobenzidine in 8.57 g of dimethyl formamide (20% w/w solution). The apparatus was immediately purged with nitrogen and the stirrer was started. To this stirred solution was added approximately 90% of a solution containing 5.97 g (0.011 mole) of BSDA in 23.87 g of dimethyl formamide (20% w/w) over a period of ten minutes, followed by addition of the remainder of the BSDA solution dropwise over a ten minute interval. The relative viscosity of the solution after the complete addition of BSDA was 70 seconds. Stirring under a nitrogen purge was continued for seven hours at which time the relative viscosity was 960 seconds (See Figure 4). The results of representative A-A-A runs using the above method are summarized in Table III.

TABLE III
A-A-A VARNISH AND FILM VISCOSITIES

Run No.	% Excess Dianhydride	% w/w Reactants in DMF	Relative Viscosity Buildup (seconds) after					η_{inh}^a DMF, 25°C
			0 hr	2 hrs	4 hrs	7 hrs	20 hrs	
27	5	25	70	120	150	----	170	0.20
30	10	25	150	260	445	2100	---	0.25
28	5	20	50	70	110	180	250	0.23
39	7	20	70	95	105	120	750	0.28
34	10	20	70	105	195	960	---	----

^aDetermined on film by redissolving after casting and drying at 50°C under vacuum. All samples contained a small amount of DMF insoluble material.

Films were cast from each of the runs described in Table III by "doctoring" A-A-A/DMF varnish solutions directly onto glass plates employing a Gardner knife. It was determined that 10-13 mil knife setting gave films of 1-2 mil thickness upon removal of DMF at 125°C for one-half hour under vacuum. A representative infrared spectrum of A-A-A film appears in Figure 5.

A.1.2.2 Preparation of Imide-Amine (IA) Film Specimens - Experimental conditions necessary for partial cure of A-A-A films to the polyimide-amine were determined employing temperatures from 200-250°C under static nitrogen and vacuum. It was found that 250°C treatment under vacuum for two hours was sufficient to remove approximately one mole of condensation water to give the desired IA stage film. These specimens were dark yellow in color and were slightly more brittle than their A-A-A precursors, but they could be creased without tearing. These film samples were insoluble in DMF.

A.1.2.3 Preparation of Pyrrone Film Specimens - The IA film strips prepared by the method above were employed to define experimental conditions that assured formation of the desired Pyrrone backbone linkages. This study employed temperatures of 300-400°C in nitrogen, air, and vacuum. It was found that heating at 360°C under vacuum for four hours gave products demonstrating the maximum degree of film flexibility coupled with complete ring closure (See infrared spectrum in Figure 5).

An indication of the strength of these crease-bendable, although rather non-uniform Pyrrone films was given by Instron tensile properties of $T/E/M_1 = 9.9 \times 10^3 \text{ psi}/4.1\%/4.1 \times 10^5 \text{ psi}$. The Pyrrone films were dark amber-red in color and insoluble in DMF. The density was determined to be 1.42 g/ml.

The Pyrrone films rapidly absorbed moisture from the air as evidenced by rapid initial weight loss on aging in air and in TGA determinations. This initial moisture loss is easily seen by referring to the film aging data in Table IV below. Experimental determinations on dry films showed a 2% moisture pickup in one hour at room temperature.

The oxidative stability of Pyrrone film sample is shown in the thermogram (TGA) appearing as Figure 7. The early weight loss in air is attributed to loss of surface moisture as discussed in the preceding paragraph. The thermo-oxidative stability of BSDA-DAB derived Pyrrone polymers to $\geq 400^\circ\text{C}$ before excessive ($>10\%$) weight loss occurred showed the potential for long term stability of Pyrrone laminates.

TABLE IV
PYRRONE FILM AGING DATA^a

Aging Temperature	Time of Aging, (Hrs)	% Weight Loss
600°F	1	2.6
	2	2.8
	4	3.2
	21	5.0
700°F	1	2.8
	2	2.9
	4	5.0

^aAll samples were aged at temperature under a 600 ml/min forced air flow

A.2 LAMINATE PROCESSING STUDIES

In the following paragraphs, representative experiments used to prepare prepregs and laminates are described. Data are summarized in tables when applicable.

A.2.1 Impregnation Studies

An A-A-A varnish solution of 20% w/w solids in DMF (~500 poise) was used to impregnate a 13-inch x 37-inch strip of Style 181 E glass cloth (coated with A-1100 amino-silane finish). The method employed hand dipping the cloth into the varnish solution and wiping once with a 0.016-inch bar gap. The prepreg was dried at 200°F for two minutes, then the prepreg was hand dipped again into the varnish with no bar gap wiping and subsequently dried for 15 minutes at 200°F. The prepreg gave the data summarized in Table V, including resin flow at 600°F under 200 psi for 30 minutes.

TABLE V
BSDA-DAB REPRESENTATIVE PREPREG DATA

Determination	Maximum %	Minimum %	Average %
Volatile Content	12.7	9.3	10.9
Resin Flow	14.5	12.7	13.6
Resin Solids	35.2	28.8	32.0

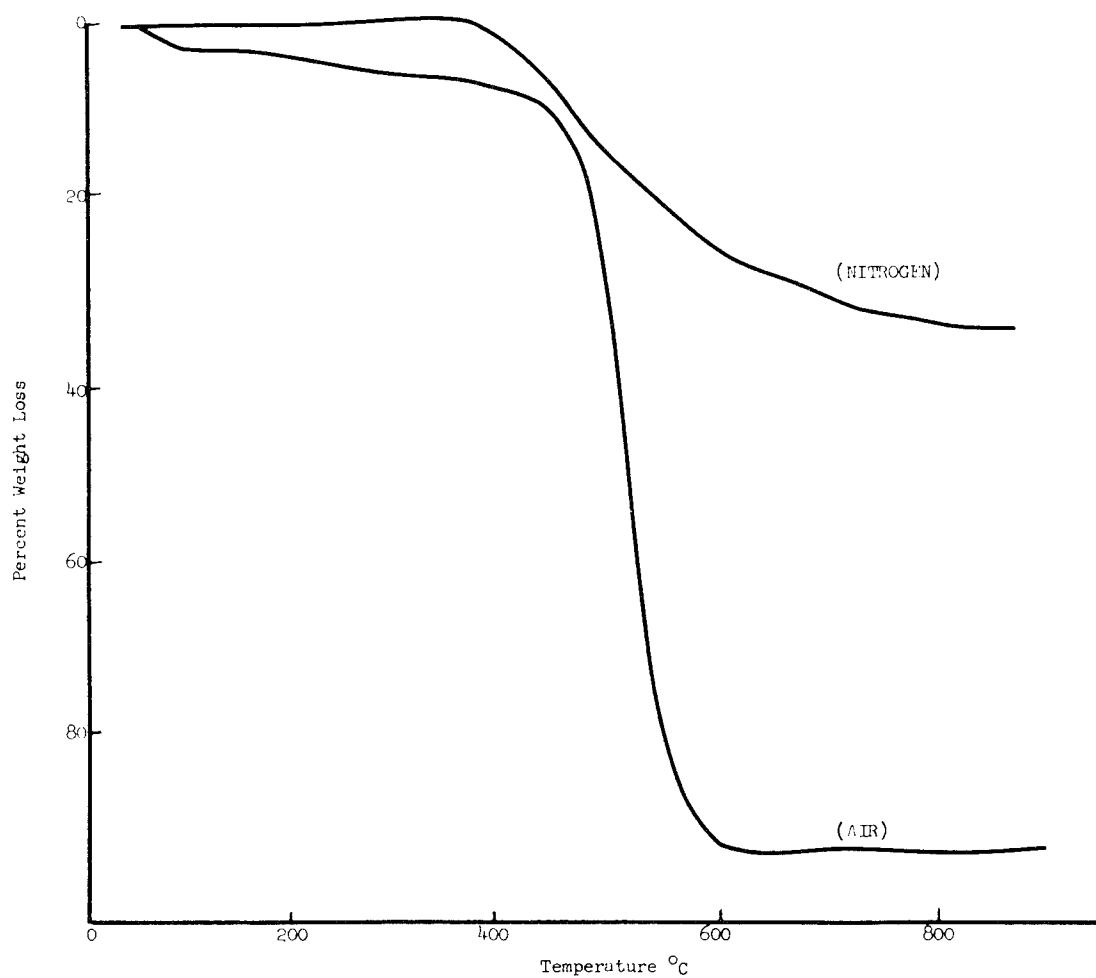


Figure 7. Thermogram of BSDA-DAB Pyrrone
Scan Rate: 3 °C/min. Gas Flow: 100 ml/min

The A-A-A impregnated Style 181 E-glass specimen was cut into thirteen 5-inch x 6-inch equally divided pieces. These prepreg pieces were used to prepare a laminate specimen as described below.

A.2.2 Laminate Processing Studies

The thirteen 5-inch x 6-inch prepreg specimens prepared as described above and characterized by the data in Table V were stacked in one layer suitable to give a 1/8-inch thick laminate structure. Thermocouple wires (8) were inserted in each corner between the first and second as well as the twelfth and thirteenth plies and the stack was stapled to ensure uniform construction and positioning of wires.

This 5-inch x 6-inch x 1/8-inch specimen was placed in the press and allowed to see a dwell time of 15 seconds at 600°F. A pressure of 200 psi was then applied for two hours at 600°F. At the end of this conditioning, the pressure was maintained at 200 psi and the temperature allowed to increase to 700°F, where in-press cure was allowed to continue for one-half hour.

The laminate specimen so prepared was allowed to cool to room temperature then the Barcol hardness was determined (62 minimum to 70 maximum). This sample was coded Specimen 2.

This specimen was cut into three equal portions. One sample was retained for the determination of properties at room temperature and the other pieces were subjected to long term aging in forced air (one each at 600°F and 700°F). Table VI below summarizes the room temperature data obtained for the unaged sample. Additional data is summarized in Table II.

TABLE VI
LAMINATE PROPERTIES FOR SPECIMEN 2

Flexural Strength $\times 10^{-3}$, psi	Flexural Modulus $\times 10^{-6}$, psi	Specific Gravity	Void Content, % v/v
53.9	2.3	1.75	16.4
48.9	3.0	1.79	14.6
56.3	2.9	1.84	12.2

This general procedure was followed to scout preparation of laminates under a variety of conditions. The processing conditions were varied to attempt to define processing and post cure conditions sufficient to allow favorable long term aging characteristics in air at 600°F and 700°F. The data describing processing and postcuring methods and laminate properties are included in Table II.

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